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## Secondary Crystallization of Isotactic Polystyrene

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### Synopsis

When isotactic polystyrene (i-PS) is crystallized from the melt or from the glassy state at rather large supercooling an additional melting peak appears on the curve during scanning in a differential calorimeter. The overall rate of crystallization deduced from the total peak areas as a function of crystallization time did not fit the Avrami equation well. When we omit the area of the additional melting peak in the kinetic analysis a much better fit is obtained. We also observed that no lamellar thickening occurs during isothermal crystallization. In view of the low degree of crystallinity of i-PS these results lead to the idea that a secondary crystallization process takes place within the amorphous parts of the spherulites resulting in this additional melting peak on the DSC curve. The large supercooling needed and the increase in peak area with increasing molecular weight make us suppose that intercrystalline links are probably responsible for the additional melting peak of bulk-crystallized i-PS. Electron microscopic studies of surface replicas of i-PS support this view.

### INTRODUCTION

Considerable effort has been devoted to the subject of secondary crystallization.<sup>1-3</sup> Owing to a difference in time dependence of primary and secondary crystallization, difficulties exist in resolving the kinetics of crystallization. By assuming that both processes are consecutive, Banks et al.<sup>1</sup> developed a method for distinguishing between the primary and secondary crystallization stage. Hillier<sup>2</sup> tried to obtain a better description of spherulitic crystallization by using a modified Avrami equation. In his model a volume element, incorporated in a spherulite during the primary crystallization stage, increases its crystallinity according to a first-order rate process. According to Sharples<sup>4</sup> we can discriminate between two possibilities for the mechanism of secondary crystallization: (i) an increase in perfection of existing crystallites during the latter stage of the total crystallization process; and (ii) crystallization of less readily crystallizable components originally rejected from the crystal growth face and trapped within spherulites. The occurrence of one or both processes during crystallization is still a matter of discussion.<sup>5,6</sup>

With i-PS we were able to study the primary and secondary crystallization stages separately with a differential calorimeter. The calorimetric data combined with electron microscopic investigations of surface replicas of i-PS were used to study the nature of secondary crystallization in i-PS.

## EXPERIMENTAL

Our i-PS sample is a sample used previously<sup>7</sup> with  $\bar{M}_n = 185 \times 10^3$  and  $\bar{M}_w = 330 \times 10^3$ . Calorimetric measurements were made on the Perkin Elmer DSC-1B. The temperature scale was calibrated at various scan speeds with metal standards. Isothermal crystallization experiments were also performed directly in the apparatus. Owing to the low crystallization rate of i-PS no prior crystallization took place during cooling from the melt or heating from the glassy state.

Small-angle x-ray measurement of bulk-crystallized i-PS were carried out with a Statton camera (Warhus Company) with  $\text{CuK}\alpha$  radiation and exposure times of 15–20 hr. The x-ray beam was collimated with two pinholes both of 0.020 in. diameter. The photographic films were scanned in a densitometer. The samples investigated were first melted under vacuum at 260°C and crystallized afterwards under pressure (the pressure slowly increased from 10 to 100 bars during isothermal crystallization) to avoid the formation of voids.

Surface replicas were made of 70/30 mixtures of i-PS and atactic polystyrene (a-PS) for electron microscopic investigations. Low molecular weight a-PS ( $\bar{M}_w = 3 \times 10^4$ ) was added to i-PS in order to obtain a more open spherulitic structure, as in the work of Keith et al.<sup>8</sup> The mixture was dissolved in dichloromethane and the solution was poured on a glass slide. After drying in air and under vacuum the film was covered with another glass slide and melted in a nitrogen atmosphere in an oven at 260°C during 10 min. This upper glass slide was necessary to obtain a flat

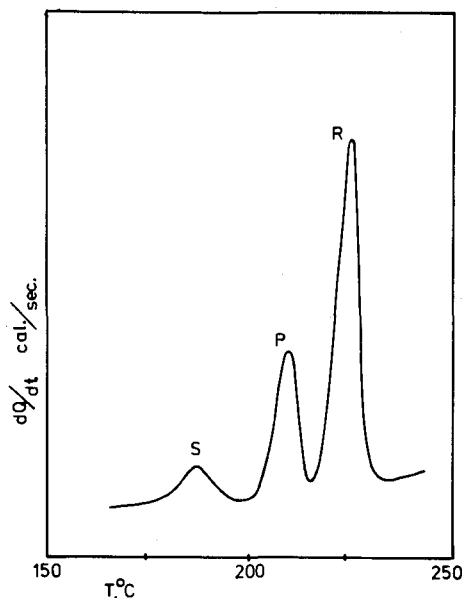


Fig. 1. DSC melting curve of isotactic polystyrene crystallized from the melt at  $T_c = 170^\circ\text{C}$ . Heating rate  $8^\circ\text{C}/\text{min}$ .

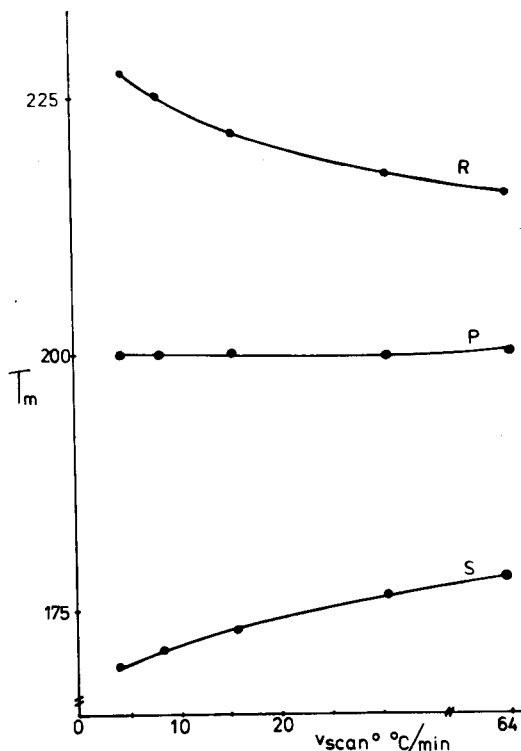


Fig. 2. Influence of DSC heating rate on the various peak temperatures of isotactic polystyrene crystallized from the melt at  $T_c = 160^\circ\text{C}$ .

homogeneous film because the polymeric mixture does not adhere well to glass and polymer droplets will form after melting if no glass cover is used. After melting, the temperature of the oven was lowered to the crystallization temperature. After crystallization for 24 hr the sample was cooled down to room temperature. At room temperature the upper glass slide could easily be detached from the nonadhering crystalline film especially when water was introduced between the slides. The a-PS was removed from the film, at least from its surface, by dipping the latter into amyl acetate which easily dissolves noncrystalline polystyrene.<sup>13</sup> In a vacuum evaporator the specimens were shadowed with platinum at an angle of  $60^\circ$  and then coated perpendicularly with carbon. The replicas were separated from the adhering polymer by dipping the specimens into hot toluene. After dissolving the polymer and cooling to room temperature, distilled water was added to the toluene and after a few minutes the replicas were located at the toluene–water interface. The upper layer of toluene was removed with a pipette and the replicas, which floated on the water surface, were picked up with grids. Electron micrographs were made with a Philips electron microscope (EM-200) at 80 kV.

## RESULTS

Figure 1 shows a typical DSC trace of i-PS crystallized from the melt at fairly large supercooling. Three melting peaks appear on the curve which we denote here by S, P, and R, respectively. The influence of heating rate on the three melting-peak temperatures is shown in Figure 2. Peak P is the normal melting peak originating from melting of lamellar crystallites whereas peak R is due to recrystallization after melting during the DSC scan.<sup>7</sup> Peak S is an additional melting peak which appears on the curve only for crystallization temperatures lower than about 190°C. When the sample is fully crystallized at  $T_c \geq 190^\circ\text{C}$ , subsequent annealing at a lower temperature, for instance 150°C, again results in this extra melting peak with a melting temperature about 20°C above the annealing temperature.

When we heat a crystallized sample beyond the melting temperature of peak S and then cool it down to the original crystallization temperature, peak S appears again on the melting curve after some time. The shapes of the peaks P and R remain unaffected during this partial melting and heating experiment.

During isothermal crystallization the melting peak temperature of peak P remains invariant with time whereas that of peak S increases by 5–8°C. Figure 3 shows the long-period spacing of melt-crystallized i-PS for different crystallization times at  $T_c = 160^\circ\text{C}$ . It demonstrates that the long-period spacing of melt-crystallized i-PS is invariant during isothermal crystallization. Figure 4 shows the area of peaks P + R and peak S as a function of time at  $T_c = 160^\circ\text{C}$ . Similar data have been reported before by Pelzbauer and Manley.<sup>9,10</sup> Table I shows the effect of molecular weight on the relative area of peak S.

From the area of the melting endotherm(s) the degree of conversion  $X$  can be calculated. Curve a in Figure 5 shows a plot of  $\log(1 - X)$  versus time on a double logarithmic scale for i-PS crystallized from the melt at 195°C. The degree of conversion fits the Avrami equation quite well with a constant value of  $n = 3$ . For this crystallization temperature no additional melting peak S appears on the DSC curve. Curve b shows the same plot for i-PS crystallized from the melt at  $T_c = 160^\circ\text{C}$ . In this case the degree of conversion is calculated from the areas of peaks P, S, and R. If

TABLE I  
The Influence of Molecular Weight on the Relative (Final) Area of Peak S for i-PS Crystallized from the Melt at 160°C

$\bar{M}_n$	Relative area/g
$30 \times 10^3$	1
$70 \times 10^3$	1.3
$85 \times 10^3$	1.6
$180 \times 10^3$	2.2
$290 \times 10^3$	2.7

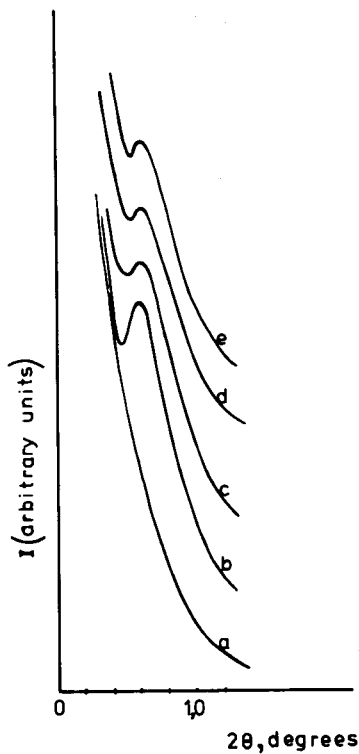


Fig. 3. Small angle x-ray scattering curves for isotactic polystyrene crystallized at 160°C during various times: (a) 15 min.; (b) 30 min.; (c) 40 min.; (d) 60 min.; (e) 300 min.

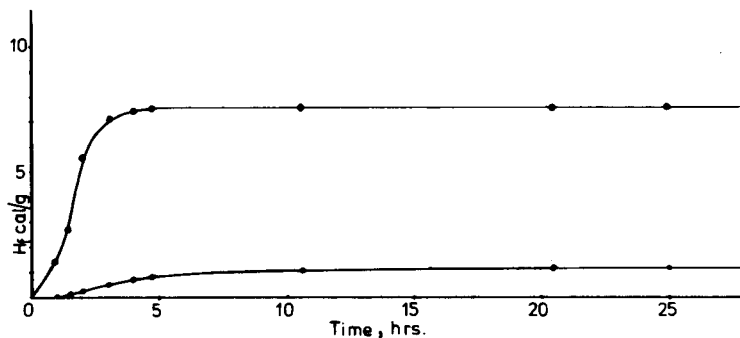


Fig. 4. Heat of melting for peak P + R (upper curve) and peak S (lower curve) of isotactic polystyrene as a function of crystallization time at  $T_c = 160^\circ\text{C}$ .

the degree of conversion is calculated from the area of peaks P and R alone a much better fit to the Avrami equation is obtained with  $n = 2.6$  (curve c).

Thin films of i-PS crystallized at 150°C were heated above the melting temperature of peak S (Fig. 6c) and then quenched to room temperature.

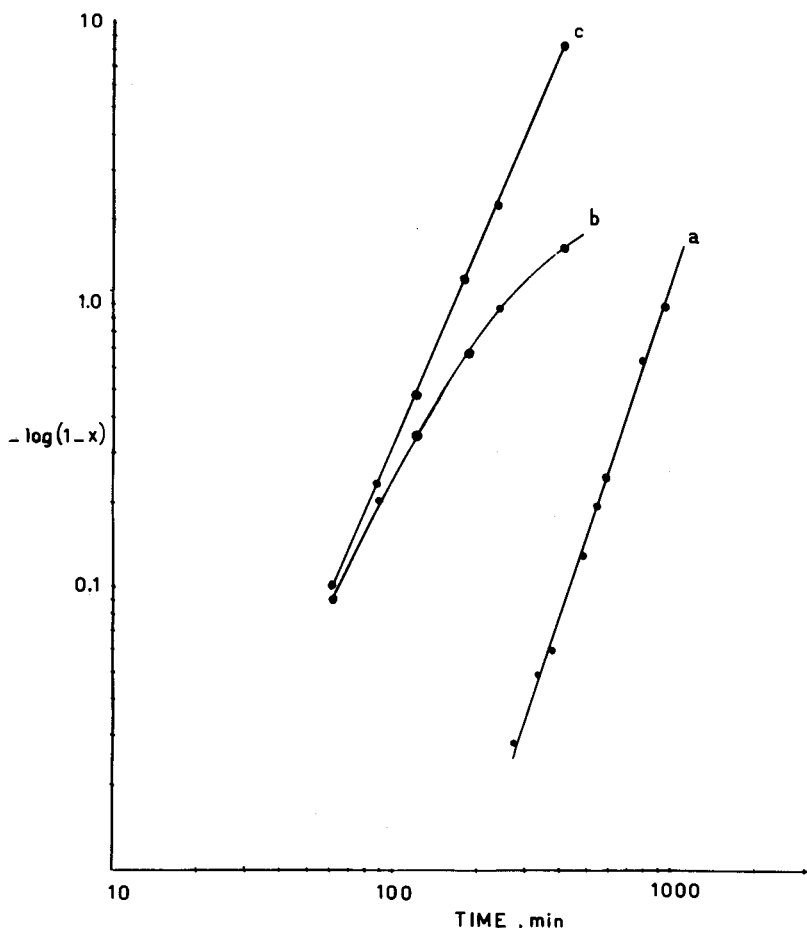


Fig. 5.  $-\log(1-X)$  vs. time for crystallization of isotactic polystyrene from the melt at: (a)  $T_c = 195^\circ\text{C}$ ; (b)  $T_c = 160^\circ\text{C}$ ; (c)  $T_c = 160^\circ\text{C}$ , corrected for secondary crystallization ( $X$  is the degree of conversion).

The DSC scan demonstrates that peak S has disappeared (Fig. 6b). These quenched films were washed for several hours with amyl acetate at room temperature with stirring. These washed films were thoroughly dried at room temperature under vacuum and next annealed at  $150^\circ\text{C}$ . The DSC scan of these washed and annealed films clearly shows peak S (Fig. 6a).

Figure 7a shows a surface replica of i-PS, crystallized at  $150^\circ\text{C}$ . Many intercrystalline links are observed connecting the lamellar crystallites. The crystalline i-PS/a-PS films from which surface replicas were made show melting behavior analogous to that of pure i-PS. When these films were heated above the melting temperature of peak S but below the melting temperature of peak P (to avoid recrystallization) the surface replicas were quite different. Only few intercrystalline links could be observed (see Fig. 7b). When these heated films were annealed at the original crystallization temperature their surface replicas again show many

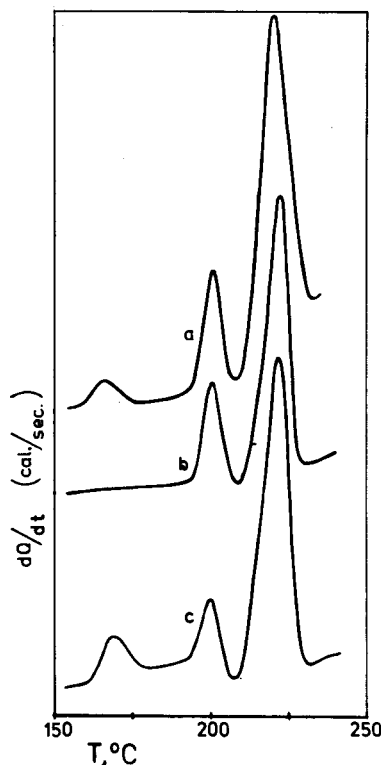


Fig. 6. DSC melting curves of bulk-crystallized isotactic polystyrene films: (c) film crystallized at 150°C; (b) the same film after heating above the peak temperature of peak S; (a) the same film as in (b) after washing with amyl acetate and subsequent annealing at 150°C.

intercrystalline links (see Fig. 7c). The replicas of crystalline films crystallized at 200°C did not show a significant number of intercrystalline links. At this crystallization temperature, peak S does not appear on the thermogram.<sup>7</sup> When crystalline films were made of i-PS/a-PS mixtures using low molecular weight i-PS ( $\bar{M}_n = 3 \times 10^4$ ), no intercrystalline links could be observed (see Fig. 8).

## DISCUSSION

From the results of the partial melting experiments we may conclude that the crystallized material corresponding to peak S on the thermogram of bulk-crystallized i-PS melts and recrystallizes independently of the rest of the crystalline i-PS. From Figure 4 we conclude that peak S originates from a slow crystallization process, which continues even after the main crystallization has been completed.

Figure 5 shows that the degree of conversion of the crystallization process based on peaks P + R only, fits the Avrami equation with a constant value of  $n$  better than the degree of conversion calculated from the total peak area P + R + S. The latter corresponds to data obtained from dilatometric



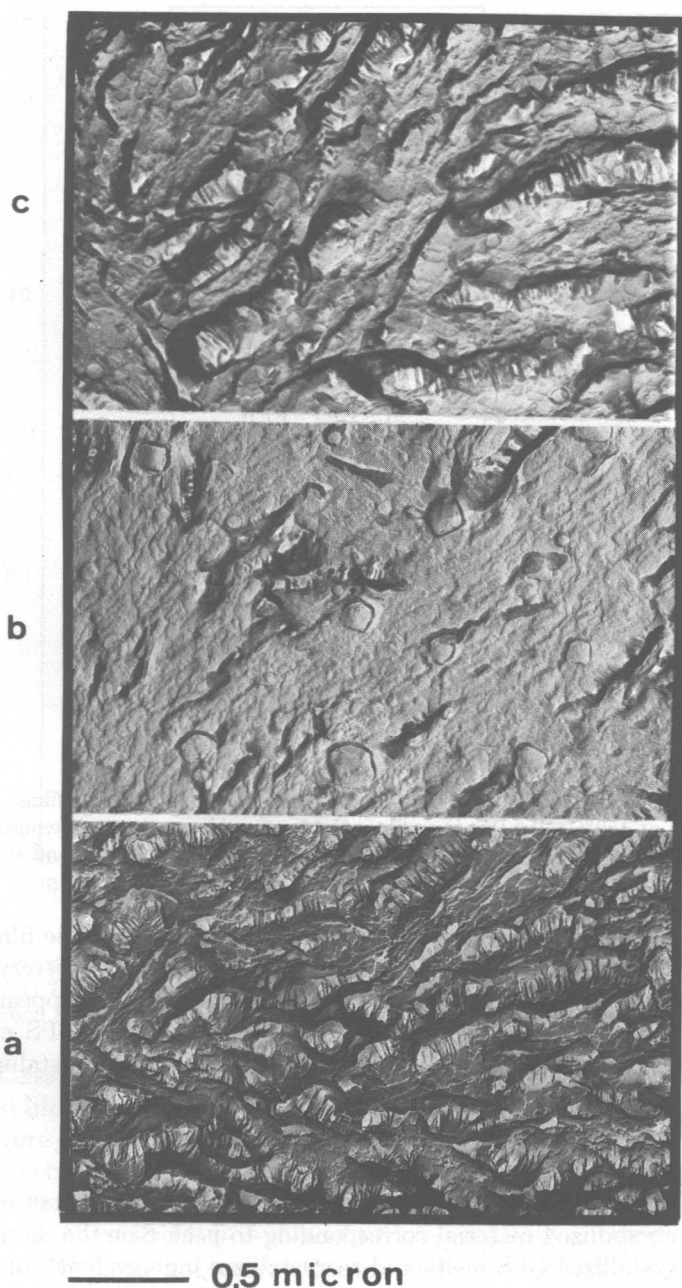


Fig. 7. Surface replicas of crystalline polystyrene films: (a) i-PS/a-PS mixture crystallized at 150°C, a-PS removed after crystallization; (b) i-PS/a-PS mixture crystallized at 150°C, then heated afterwards to 190°C (beyond peak S) after which a-PS was removed; (c) i-PS/a-PS mixture crystallized at 150°C, then heated to 190°C, reannealed at 150°C for 24 hr, after which a-PS was removed.

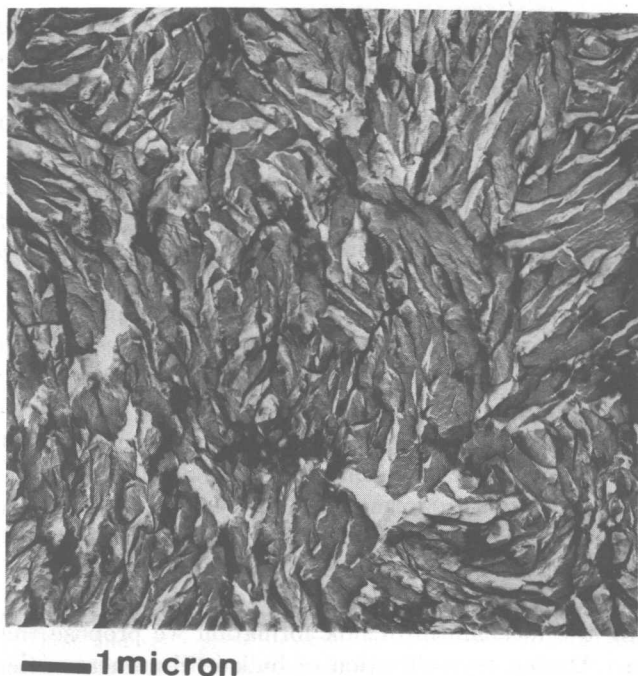


Fig. 8. Surface replica of crystalline low molecular weight isotactic polystyrene film ( $\bar{M}_n = 3 \times 10^4$ ) crystallized at 150°C. After crystallization the diluent *a*-PS was removed.

experiments and requires decreasing  $n$  in the latter stage of the crystallization process.<sup>11</sup>

From Fig. 3 and the constant melting temperature of peak P during isothermal crystallization, we conclude that the lamellar fold period does not change during isothermal crystallization. This is easy to understand since *i*-PS is a very slowly crystallizing polymer with bulky side groups, for which isothermal thickening of lamellae is not to be expected.

The foregoing prompts us to distinguish between a primary crystallization process giving rise to peak P (and by recrystallization to peak R) and a secondary crystallization process between the lamellae resulting in the additional melting peak S.\*

\* Regarding the origin of this secondary crystallization process, we have taken into account the possibilities that low molecular weight or less stereoregular species in the sample, due to a lower rate of crystallization, cause this slow interlamellar crystallization. We investigated the spherulitic growth rate of *i*-PS as a function of molecular weight<sup>12</sup> and we found that the growth rate increased rather than decreased with decreasing molecular weight in the range investigated  $3 \times 10^4 < \bar{M}_n < 3 \times 10^5$ . Since the sample used here does not contain a significant weight fraction of molecules with  $\bar{M}_n < 3 \times 10^4$ , we rejected the possibility that low molecular weight *i*-PS causes peak S. On the contrary it appeared that high molecular weight species promote peak S (see Table I). In a previous paper<sup>7</sup> it was already reported that *i*-PS freed from possible less stereoregular material by crystallization from very dilute solution can still produce the extra melting peak S.

The results in Figure 6 indicate that the material corresponding to peak S cannot be removed after melting by dissolving in amyl acetate, which is known to dissolve amorphous i-PS easily from the "crystalline frame."<sup>13</sup> So we conclude that the material corresponding to peak S is connected to the "crystalline frame" in some way. The increase of peak area with increasing molecular weight (Table I) and the appearance of S on the thermogram only at fairly large supercooling leads us to suggest that intercrystalline links may be responsible for the appearance of peak S on the thermogram of bulk-crystallized i-PS.

Figure 7 shows the presence of many intercrystalline links. Although the surface replicas were taken from i-PS/a-PS mixtures in order to obtain a more open spherulitic structure, these links are expected to be present in pure i-PS too. The influence of thermal history on the number of intercrystalline links (see Fig. 7) confirms the idea that melting of these links causes peak S. When low molecular weight i-PS is used ( $\bar{M}_n = 30 \times 10^3$ ) no intercrystalline links are formed during crystallization of the i-PS/a-PS mixture (see Fig. 8). In this case the i-PS molecules are too short to become incorporated in different lamellae and the thermogram of this crystallized mixture does not show the peak S.\*

Regarding the mechanism of link formation we propose the following mechanism. During crystallization of bulk i-PS numerous tie molecules are formed especially at rather large supercooling. These tie molecules can aggregate locally to form intercrystalline links. The links consist of a small number of tie molecules.

\* It might seem likely that during removal of a-PS (from the surface of the crystallized films before replicas are made), artifacts would be introduced by local swelling prior to dissolution and appear as intercrystalline links. However, mixtures of i-PS with a low molecular weight substance, like dioctyl phthalate, also show intercrystalline links.

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